

FINAL TECHNICAL REPORT

Long-Lived, Energetic States of Small Molecules: Spectroscopy, Pattern Recognition, and Formation/Destruction Mechanisms

**Air Force Office of Scientific Research
Grant Number F49620-01-1-0078**

Principal Investigator : Robert W. Field

Massachusetts Institute of Technology
Department of Chemistry
77 Massachusetts Avenue
Cambridge, Massachusetts 02139-4307

20041119 012

Period Covered: 01 December 00 - 30 June 2004

REPORT DOCUMENTATION PAGE

AFRL-SR-AR-TR-04

0570

Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, gathering existing data needed, and completing and reviewing this collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden to Washington Headquarters Services, Directorate for Information Operations and Reports (0704-0188) 4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to any penalty for failing to comply with a collection of information if it does not have a valid OMB control number. PLEASE DO NOT RETURN YOUR FORM TO THE ABOVE ADDRESS.

| | | | | | |
|--|-----------------------------|-----------------------------------|----------------------------|---|---|
| 1. REPORT DATE (DD-MM-YYYY) 10-11-2004 | | 2. REPORT TYPE Final Technical | | 3. DATES COVERED (from - to) 12/01/00 - 06/30/04 | |
| 4. TITLE AND SUBTITLE Long-Lived, Energetic States of Small Molecules: Spectroscopy, Pattern Recognition, and Formation/Destruction mechanisms | | | | 5a. CONTRACT NUMBER | |
| | | | | 5b. GRANT NUMBER AFOSR-F49620-01-1-0078 | |
| | | | | 5c. PROGRAM ELEMENT NUMBER | |
| 6. AUTHOR(S) Professor Robert W. Field | | | | 5d. PROJECT NUMBER | |
| | | | | 5e. TASK NUMBER 2303/ES | |
| | | | | 5f. WORK UNIT NUMBER | |
| 7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Massachusetts Institute of Technology 77 Massachusetts Avenue, Room 6-219 Cambridge, MA 02139-4307 | | | | 8. PERFORMING ORGANIZATION REPORT NUMBER | |
| 9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES) NL | | | | 10. SPONSOR/MONITOR'S ACRONYM(S) | |
| | | | | 11. SPONSOR/MONITOR'S REPORT NUMBER(S) | |
| 12. DISTRIBUTION / AVAILABILITY STATEMENT Approve for Public Release:Distribution Unlimited | | | | | |
| 13. SUPPLEMENTARY NOTES | | | | | |
| 14. ABSTRACT The formation, deactivation, and detection mechanisms of atoms and molecules in metastable electronically excited states are, in general, ill characterized. Yet the chemical and photophysical properties of such states are relevant to Air Force Missions in communication, upper atmosphere modeling, and high-speed vehicle tracking, and identification. The capabilities of a multispectral molecular beam apparatus have been demonstrated on the electronic spectrum of acetylene in the energy region of the first excited singlet state (S_1), which is isoenergetic with high vibrational levels of the metastable triplet states (T_1 , T_2 , T_3). This apparatus records two kinds of spectra (UV-LIF and SEELEM, respectively UltraViolet Laser Induced Fluorescence and Surface Electron Ejection by Laser Excited Metastables) simultaneously, which sample complementary groups of short- and long-lived rovibronic states. The most remarkable findings are: (i) UV-LIF spectra contain fully assignable eigenstates with dominant S_1 or T_3 character, where the T_3 character acts as a "doorway" into states of dominant T_1 , T_2 character that appear in SEELEM spectra; (ii) SEELEM spectra contain eigenstates that are rotationally fully assignable, regular in level pattern and relative intensity, yet <i>vibrationally ergodic</i> . Ergodicity in T_{23} coexists with doorway behavior in T_1 . Ergodicity, contrary to naive expectations, results in regular appearing spectra. | | | | | |
| 15. SUBJECT TERMS | | | | | |
| 16. SECURITY CLASSIFICATION OF: | | | 17. LIMITATION OF ABSTRACT | 18. NUMBER OF PAGES | 19a. NAME OF RESPONSIBLE PERSON Robert w. Field |
| a. REPORT unclassified | b. ABSTRACT unclassified | c. THIS PAGE unclassified | | | 19b. TELEPHONE NUMBER (include area code) 617-253-1489 |

I. STAFF SUPPORTED BY AFOSR GRANT

A. Postdocs

1. Adya P. Mishra, currently Scientific Research Officer, Bhabha Atomic Research Centre, India
2. Daniel S. Byun, currently Staff Assistant, Lam Research

B. Graduate Students

1. Ryan Thom (Ph.D. expected 8/05)
2. Kyle Bittinger
3. Serhan N. Altunata (Ph.D. expected 8/05)
4. Selen Altunata (Ph.D. 8/01, currently Staff Scientist, IGEN International)

C. Undergraduate Students

1. Jessica Hagelstein
2. Atanas Pavlov
3. Shervin Fatehi (currently, Ph.D. student, Berkeley)

D. Visiting Scientists

1. Margaret Fackler (summer visiting graduate student, currently, Ph.D. student, University of Texas)
2. Stephen Coy (consultant)
3. Matijs De Groot (visiting graduate student from University of Amsterdam, The Netherlands)

E. Collaborators

1. David Chandler (Combustion Research Laboratory, Sandia, Livermore)
2. Jingsong Zhang (University of California, Riverside)
3. Hideto Kanamori (Tokyo Institute of Technology)
4. Charles Pibel (American University)
5. Timothy Zwier (Purdue University)
6. Marsha Lester (University of Pennsylvania)
7. Wybren Buma (University of Amsterdam)
8. Steven J. Lipson (AFRL/VSBT)
9. James A. Dodd (AFRL/VSBT)
10. Steven M. Miller (AFRL/VSBT)
11. Skip Williams (AFRL/VSBT)

II. Research Accomplishments

(1 December 2000 - 30 June 2004)

The following is a slightly edited version of the Accomplishments section (and cited References) of the 3-year Renewal Proposal, submitted in February, 2004, and currently under consideration for support by the AFOSR.

A. Objectives

The objectives of the project "Long-Lived, Energetic States of Small Molecules: Spectroscopy, Pattern-Recognition, and Formation/Destruction Mechanisms" have been to develop experimental methods and analysis techniques in order to detect small molecules in long-lived ($\tau > 100\mu\text{s}$) electronically excited states and to determine their structure and excitation, detection, and decay mechanisms. Acetylene has served as the initial test molecule in all completed experiments.

B. Accomplishments

A multispectral, pulsed supersonic-jet, molecular-beam apparatus has been constructed, tested, and refined.^[2-4] Three complementary signal channels are simultaneously recorded: Ultraviolet fluorescence detected Laser Induced Fluorescence (UV-LIF), Time-of-Flight Surface Electron Emission by Laser Excited Metastable molecules (TOF-SEELEM), and LIF detected by infrared fluorescence from photofragments (IR-LIF). The UV-LIF channel detects transitions that terminate in an eigenstate that fluoresces in the near UV with radiative lifetime $< 30\mu\text{s}$ (see Figure 3). The SEELEM channel detects transitions that terminate in an eigenstate that has a vertical excitation energy larger than the work function of the SEELEM detector surface (Au 5.1 eV or Cs 2.1 eV) and remains electronically excited for a time comparable to the $100\mu\text{s}$ transit time from excitation region to detector surface. No eigenstate can appear in both UV-LIF and SEELEM spectra. The TOF capability distinguishes between SEELEM signals from metastable photofragments and metastable parent molecules.^[2] The signal in the IR-LIF channel arises from electronically excited photofragments produced by a two-photon transition, resonant at the one-photon level with a singlet-triplet mixed eigenstate in the parent molecule and resonant at the two-photon level with a predissociated singlet or triplet Rydberg state. The IR-LIF channel is capable of measuring the fractional singlet or triplet character in each eigenstate.

A general expression for the sampled molecular eigenstates is

$$\psi_j = \alpha_{j,S_1,\tilde{v}}\psi_{S_1,\tilde{v}} + \beta_{j,T_3,F_i,\tilde{v}}\psi_{T_3,F_i,\tilde{v}} + \sum_{\tilde{v}} \gamma_{j,T_1,F_i,\tilde{v}}\psi_{T_1,F_i,\tilde{v}}$$

where α , β , γ are mixing coefficients, S_1 means first excited singlet state, \tilde{v} is the set of vibrational quantum numbers, T_3 is an excited triplet state, T_1 is the lowest triplet state, and F_i is the spin-component of a triplet state. When the α , β , γ mixing coefficients for all spectroscopically accessed eigenstates in the explored energy region are measured in our multispectral apparatus, a complete effective Hamiltonian model of the $S_1 \leftrightarrow T_3 \leftrightarrow T_1$ dynamics is obtained.

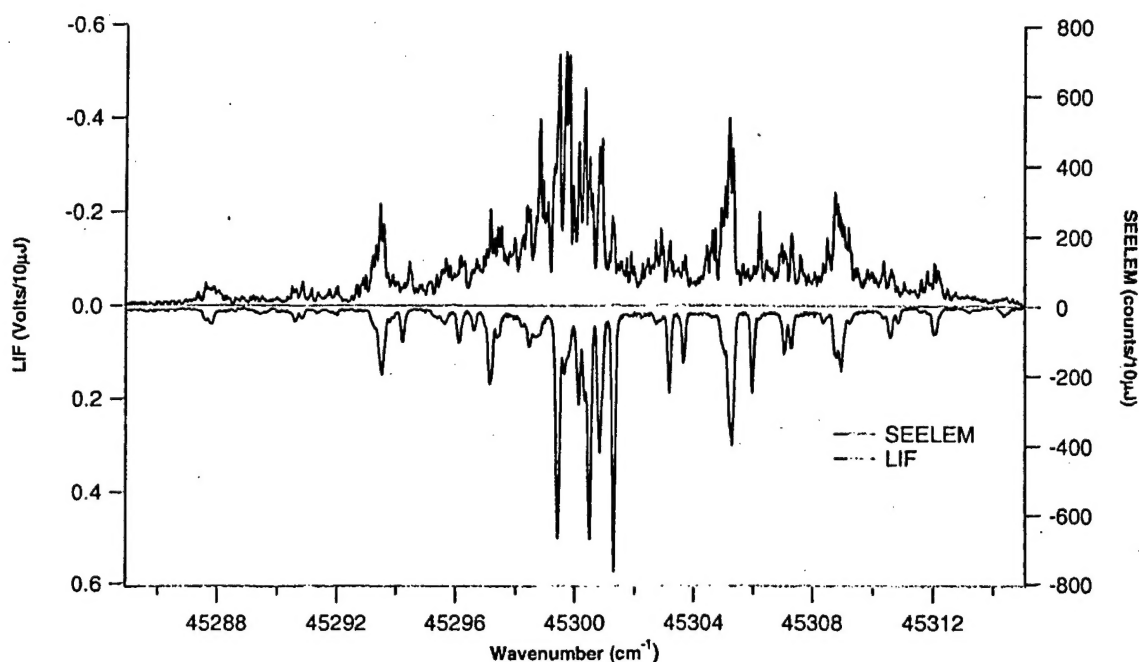


Figure 1: Simultaneously recorded SEELEM (upper trace) and UV-LIF (lower trace) spectra of the HCCH $\tilde{A} - \tilde{X} V_0 K_0^1$ sub-band. The resolution in the SEELEM spectrum is 0.03 cm^{-1} , a factor of 3 superior to that in the UV-LIF spectrum. The spectra are plotted on a compressed wavenumber scale, which emphasizes their similarity. Although no upper eigenstate appears in both spectra, the $10\times$ more densely-spaced spectral lines in the SEELEM spectrum appear within narrow windows surrounding each line in the UV-LIF spectrum.

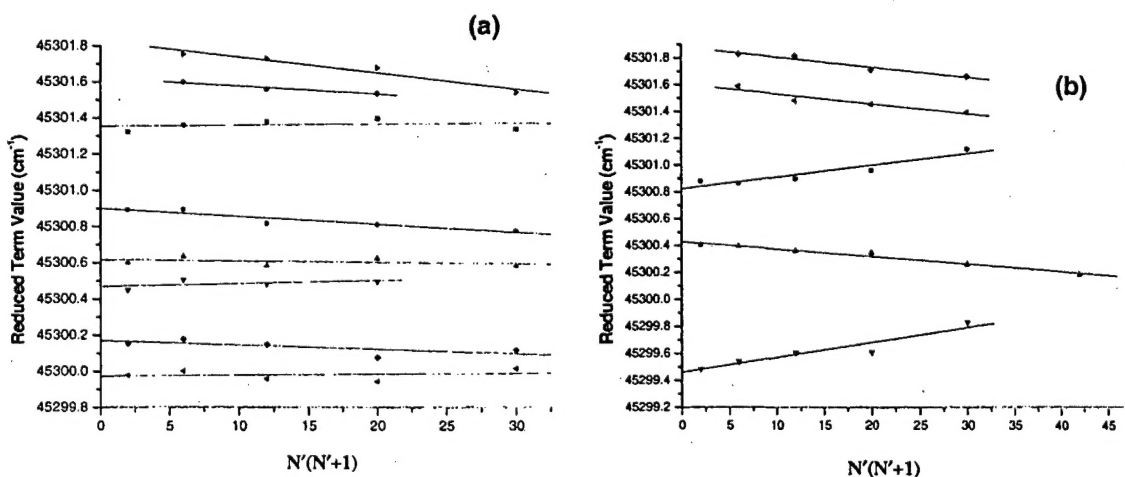


Figure 2: Reduced rotational term value ($E - \bar{B}N'(N' + 1)$, $\bar{B} = 1.127 \text{ cm}^{-1}$) plots of triplet state vibrational levels plotted vs. $N'(N' + 1)$. The term values in (a) are e-symmetry levels sampled via R,P branch transitions; those in (b) are f-symmetry levels sampled via Q-branch transitions. The observed vibrational density of states in the SEELEM spectrum is $1.2 \text{ states/cm}^{-1}$ and the calculated total symmetry-sorted density of T_1 , T_2 , T_3 vibrational states is $1.6 \text{ states/cm}^{-1}$.

The ability to distinguish excited triplet from lowest lying triplet state (T_3 vs. T_1) characters is critical to being able to construct a complete (S_1 , T_3 , T_1) dynamical model. This capability was demonstrated by comparing the absolute signal (counts per laser pulse) when the same region of the SEELEM spectrum was recorded on Yttrium (3.1 eV) and Cesium (2.1 eV) surfaces.^[3] In HCCH, only S_1 and T_3 characters in an eigenstate are detectable on a Yttrium surface whereas S_1 , T_3 , T_2 , T_1 characters are detectable on a

Cesium surface. In the energy region examined, the vibrational density of T_1 , T_2 states is 10^3 times larger than that on S_1 , T_3 . The SEELEM spectrum recorded on Cs is 800 times stronger than that on Y.^[3] In addition, the relative intensities of features in the two spectra are different, owing to the fact that $T_{1,2}$ are "bright" on Cs but not on Y.

The dynamic range in our Au-SEELEM spectra is $> 10^4$.^[4] It turns out that this is sufficient to detect transitions into at least 1/3 of all vibronic-symmetry accessible T_1 , T_2 vibrational levels that occur within a $\sim 2 \text{ cm}^{-1}$ window surrounding each S_1 $3\nu_3$ $K = 1$ level (see Figure 4).^[4] Although most of the detected eigenstates are of predominant $T_{1,2}$ character ($> 99.9\%$), the minuscule admixtures of S_1 and T_3 character renders these eigenstates Au-SEELEM detectable. The spin-orbit matrix elements responsible for mixing S_1 , T_3 character into predominantly T_1 , T_2 states include a vibrational overlap integral as a multiplicative factor.^[13] The vast majority of vibrational overlap integrals between highly excited vibrational levels of one potential surface and low vibrational levels of another, similarly shaped surface, are $\ll 10^{-3}$. Our observation of $\sim 1/3$ of the T_1 , T_2 vibrational levels in the Au-SEELEM spectrum implies that anharmonic mixing on the T_1 surface is close to the ergodic limit at $E_{\text{VIB}} = 12,000 \text{ cm}^{-1}$.^[4] This is the strongest spectroscopic evidence ever obtained for ergodic vibrational behavior in a small (4-atom-dihydride) molecule.

But it turns out that these near-ergodic SEELEM spectra are spin-rotationally (J , K_a , N , e/f -symmetry) assignable.^[4] Despite the ~ 10 lines per cm^{-1} in the SEELEM spectra, the vast majority of transitions are assignable using the "lower-state rotational combination difference" method. The assigned rotational levels fall onto smooth, linear, non-intersecting E_J vs. $BJ(J+1)$ term energy plots (see Figure 4) and on linear $\ln(I_J)$ vs. $BJ(J+1)$ Boltzmann intensity plots. Despite the near-ergodic limit mixing of vibrational characters, the rotational levels seem to arrange themselves into smooth, local-perturbation-free "vibrational levels." This combination of vibrational ergodicity and rotational regularity is without precedent.

High resolution is critically important in being able to detect weak lines near strong lines (dynamic range) and in being able to make reliable rotational assignments by the combination difference method. The use of an injection-seeded Nd:YAG laser to excite our dye laser led to a factor of ~ 3 improvement in dye laser resolution ($\sim 0.03 \text{ cm}^{-1}$ in the UV).^[4] This factor of 3 is the difference between spectra that could at best be subjected to statistical measures^[135,136] to spectra that can be unambiguously assigned. Another factor of 10 in resolution will soon be available (Coherent 899-29 cw Ti:Sapphire laser at 840 nm cw-doubled in a Spectra Physics WaveTrain to 420 nm and then pulse-amplified and doubled again to 210 nm). We expect this will improve both dynamic range and reliability of rotational assignment and also permit extension of 0.003 cm^{-1} resolution SEELEM spectroscopy to larger molecules.

The dynamic range of the UV-LIF spectrum is also $\sim 10^4$. This has enabled detection of $S_1 \leftarrow S_0$ transitions into previously unobserved vibrational levels of the HCCH S_1 state.^[4] Recently, the laser excitation and fluorescence viewing region was moved from the upstream to the downstream side of the skimmer that separates the source from the detector chamber. The resolution went from Doppler-limited 0.08 cm^{-1} upstream to laser-limited 0.03 cm^{-1} downstream. Although the currently achieved 0.03 cm^{-1} resolution in our UV-LIF spectrum is inferior to that achieved by Drabbels *et al.*,^[137] Figure 5 shows how each improvement of resolution uncovers additional assignable features. A wealth of new information is now laid bare in the UV-LIF spectrum.

C. Collaborations with Research Groups at Air Force Laboratories

We have collaborated with the research group of James A. Dodd (AFRL/VSBT) on the mechanism of predissociation of the OH $B^2\Sigma^+$ state. Owing to the peculiar shape of the B-state potential curve, LIF monitoring of populations in vibrational levels, v'' , of the OH $X^2\Pi_1$ state via the B-X transition is far more flexible than via the more familiar and extensively used A-X transition. The reason for this is that Franck-Condon factors for B-X ($v' = 0, v''$) transitions permit monitoring of all v' up to at least $v'' = 10$, whereas those for the A-X transition restrict observations to $v'' < 4$. The unique (v' , J' , F'_1)-dependent pattern of predissociation rates in the B-state implicates spin-orbit and rotation-electronic interactions with the continuum of the $2^2\Pi$ state as the primary predissociation mechanism. A detailed semi-empirical analysis of the signature of predissociation of a $2^2\Sigma^+$ state by the continuum of a $2^2\Pi$ state is presented. Relationships are derived between spin-orbit and L-uncoupling interaction parameters, with particular relevance to the electronic configurations of diatomic monohydride molecules.

A collaboration with the research group of Steven M. Miller (AFRL/VSBM) concerning analysis of some perturbations involving the NO $B^2\Pi$, $C^2\Pi$, and $a^4\Pi$ states is under discussion. A nonlinear least squares deperturbation-fitting program, developed by the PIs research group, has been provided (with tutorial in its use) to the Miller group. Possibilities for experiments based on Hg-photosensitized population of the NO $a^4\Pi$ state have been discussed.

There have been discussions, with Dr. Skip Williams (AFRL/VSBXT), of the feasibility and relative merits of various ultra-sensitive optical detection schemes for the O_2 $a^1\Delta_g$ state. It quickly became clear that direct absorption studies via the electric dipole forbidden, electric quadrupole allowed $b^1\Sigma_g^+ \leftarrow a^1\Delta_g$ transition are the best candidate for the required absolute number density measurements. The extant spectroscopic data concerning the $b^1\Sigma_g^+ \leftarrow a^1\Delta_g$ electronic states was examined and found to be of extremely high quality (completeness of states studied, wavenumber precision, reliability of analyses) and free of arcane details that would require knowledge of spectroscopic perturbations and nonstandard effective Hamiltonian models. Two *ab initio* quantum chemical theorists, who use contrasting methods to obtain state-of-the-art quality results, were proposed as likely to be able to compute quadrupole transition probabilities at an accuracy competitive with the most accurate experimental methods: David Yarkony (Johns Hopkins University) and John Stanton (University of Texas). Advice is being provided to Dr. Williams concerning the spectroscopy, rotational line strengths, and Franck-Condon factors for the O_2 $b^1\Sigma_g^+ \leftarrow a^1\Delta_g$ transition.

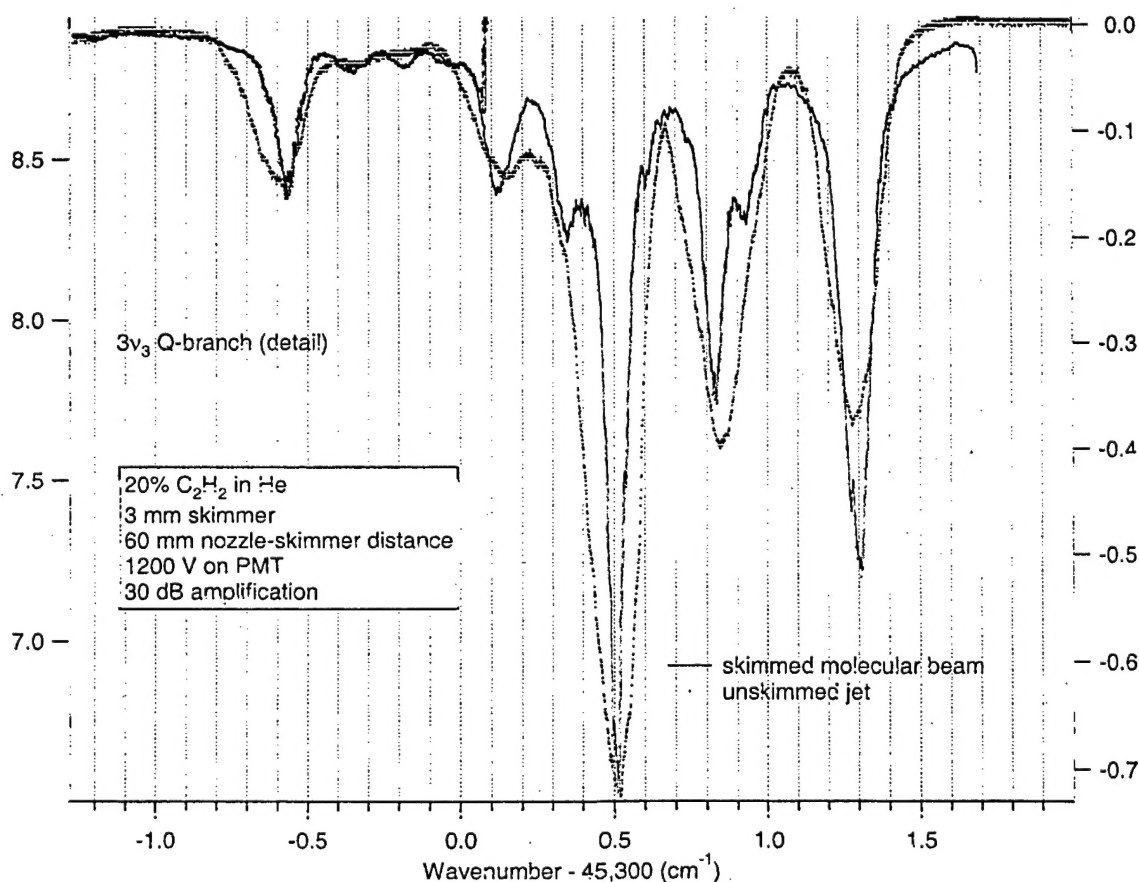


Figure 3: Segment of the UV-LIF spectrum in the $HCCH \tilde{A} - \tilde{X} V_0^3 K_0^1$ band. Dotted curve shows Doppler broadened spectrum of unskimmed jet. Solid curve shows laser linewidth limited (0.03 cm^{-1}) spectrum of skimmed (3mm diameter skimmer, 60mm nozzle-skimmer distance) molecular beam.

D. References

1. O. Sne and O. Cheshnovsky, "Surface Ejection of Electrons by Laser-Excited Metastables of Anthracene Derivatives," *Chem. Phys. Lett.* **130**, 53-58 (1986); O. Sne and O. Cheshnovsky, "Long Radiative Lifetimes of SO₂ in a Collision-Free Supersonic Molecular Beam," *Chem. Phys. Lett.* **130**, 487-492 (1986); O. Sne and O. Cheshnovsky, "Triplet Selectivity in Surface Ejection of Electrons by Laser-Excited Metastables of Aniline," *Chem. Phys. Lett.* **146**, 216-220 (1988); O. Sne and O. Cheshnovsky, "Dynamics of Triplet States in Beam-Isolated Benzaldehyde," *J. Phys. Chem.* **95**, 7154-7164 (1991);
2. S.J. Humphrey, C.G. Morgan, A.M. Wodtke, K.L. Cunningham, S. Drucker, and R.W. Field, "Laser Excited Metastable States of Acetylene in the 5.5 - 5.7 eV Region," *J. Chem. Phys.* **107**, 49-53 (1997).
3. S. Altunata, K. L. Cunningham, M. Canagaratna, R. Thom and R. W. Field, "The Mechanism of Surface Electron Ejection by Laser Excited Metastable Molecules," *J. Phys. Chem.* **106**, 1122-1130 (2002).
4. A. P. Mishra, R. L. Thom, and R. W. Field, "Ultraviolet Laser Induced Fluorescence and Surface Electron Ejection by Laser Excited Metastables Spectroscopy of Acetylene in the Vicinity of the $\tilde{A} - \tilde{X}$ V₀³ K₀¹ Band," *J. Mol. Spectrosc.*, submitted.
5. H. E. Hunziker, "A New Technique for Gas-Phase Kinetic Spectroscopy of Molecules in the Triplet State," *IBM. J. Res. Develop.* **15**, 10-26 (1971).
6. A. B. Burrill, J. T. Zhou, and P. M. Johnson, "Mass-Analyzed Threshold Ionization Spectra of C₆H₆⁺ and C₆D₆⁺ Obtained via the ³B_{1u} Triplet State," *J. Phys. Chem. A* **107**, 4601-4606 (2003).
7. T. J. Gay, "Sources of Metastable Atoms and Molecules," pp. 95-114 in *Atomic, Molecular, and Optical Physics: Atoms and Molecules*, Vol. 29B *Experimental Methods in The Physical Sciences* (eds. F. B. Dunning and R. G. Hulet), Academic, 1996.
8. H. Hagstrum, "Theory of Auger Ejection of Electrons from Metals by Ions," *Phys. Rev.* **96**, 336-365 (1954).
9. H. Hotop, "Detection of Metastable Atoms and Molecules, pp. 191-215 in, *Experimental Methods in The Physical Sciences*, vol. 29B, (Atomic, Molecular and Optical Physics: Atoms and Molecules, ed. F. B. Dunning and R. G. Hulet), Academic, 1996.
10. R. T. Jongma, G. Berden, T. Rasing, H. Zacharias, and G. Meijer, "State-to-State Scattering of Metastable CO Molecules from a LiF(100) Surface," *J. Chem. Phys.* **107**, 252-261 (1997); *ibid*, "Scattering of Vibrationally and Electronically Excited CO Molecules from a LiF(100) Surface," *Chem. Phys. Lett.* **273**, 147-152 (1997).
11. R.W. Field, B.G. Wicke, J.D. Simmons and S.G. Tilford, "Analysis of Perturbations in the a³Π and A¹Π States of CO", *J. Mol. Spectrosc.* **44**, 383-399 (1972).
12. F. Rostas, M. Eidelsberg, A. Jolly, J. L. Lemaire, A. Le Floch, and J. Rostas, "Band Oscillator Strengths of the Intersystem Transitions of CO", *J. Chem. Phys.* **112**, 4591-4603 (2000).
13. H. Lefebvre-Brion and R. W. Field, "The Spectra and Dynamics of Diatomic Molecules," Elsevier, 2004.
14. G. Cario and J. Franck, "Über Zerlegung von Wasserstoffmolekülen durch angeregte Quecksilberatome," *Z. Phys.* **11**, 161-166 (1922); K. J. Laidler, "The Mechanism of Processes Initiated by Excited Atoms. III. Photo-Sensitized Hydrocarbon Reactions," *J. Chem. Phys.* **15**, 712-726 (1947); H. Okabe, pp. 139-161, in *Photochemistry of Small Molecules*, Wiley, New York, 1978.
15. S. H. Brown and R. H. Crabtree, "Alkane Activation with Mercury Vapor," *J. Chem. Edu.* **65**, 290-294 (1988); R. H. Crabtree, S. H. Brown, C. A. Muedas, P. Krajnik, and R. R. Ferguson, "Recent Advances in Mercury Photosensitized Reactions," *J. Molec. Catalysis* **74**, 85-95 (1992).

16. J. L. Tomer, K. W. Holtzclaw, and D. W. Pratt, "Phosphorescence Excitation Spectroscopy in Supersonic Jets. The Lowest Triplet-State of Pyrazine," *J. Chem. Phys.* **88**, 1528-1535 (1988); L.H. Spangler and D.W. Pratt, "Laser-Induced Phosphorescence Spectroscopy in Supersonic Jets. The Lowest Triplet-States of Glyoxal, Methylglyoxal, and Biacetyl," *J. Chem. Phys.* **84**, 4789-4796 (1986).
17. T. Suzuki, Y. Shi, H. Kohguchi, "Detection of Metastable Triplet Acetylene Produced by Intersystem Crossing from the Excited $\tilde{A}(^1A_u)$ State," *J. Chem. Phys.* **106**, 5292-5295 (1997); Y. Shi and T. Suzuki, "Formation of Metastable Triplet Acetylene from the $\tilde{A}(^1A_u)$ State Near the Dissociation Threshold," *J. Phys. Chem. A* **102**, 7414-7419 (1998).
18. C. Kittrell, E. Abramson, J.L. Kinsey, S. McDonald, D.E. Reisner, D. Katayama, and R.W. Field, "Selective Vibrational Excitation by Stimulated Emission Pumping", *J. Chem. Phys.* **75**, 2056-2059 (1981)
19. Li Li and R.W. Field, "Direct Observation of High-Lying $^3\Pi_g$ States of the Na_2 Molecule by Optical-Optical Double Resonance," *J. Phys. Chem.* **87**, 3020-3022 (1983).
20. T. G. Dietz, M. A. Duncan, D. E. Powers, and R. E. Smalley, "Laser Production of Supersonic Metal Cluster Beams," *J. Chem. Phys.* **74**, 6511-6512 (1981); J. B. Hopkins, P. R. R. Langridge-Smith, M. D. Morse, and R. E. Smalley, "Supersonic Metal Cluster Beams of Refractory Metals: Spectral Investigations of Ultracold Mo_2 ," *J. Chem. Phys.* **78**, 1627-1637 (1983).
21. M. D. Morse, "Supersonic Beam Sources," pp. 21-47 in Atomic, Molecular, and Optical Physics: Atoms and Molecules, Vol. 29B (ed. F. B. Dunning and R. G. Hulet), Academic, 1996.
22. K. Bier and O. Hagena, "Optimum Conditions for Generating Supersonic Molecular Beams," pp. 260-278 in Rarefied Gas Dynamics, Vol. 2 (ed. J. H. de Leeuw), Academic, 1963.
23. W. M. McClain and R. A. Harris, "Two-Photon Molecular Spectroscopy in Liquids and Gases", pp. 1-55 in Excited States, vol. 3, ed. E. C. Lin, Academic, New York, 1978; K. D. Bonin and T. J. McIlrath, "Two-Photon Electric-Dipole Selection Rules," *J. Opt. Soc. Am. B* **1**, 52-55 (1984).
24. J. A. Haberman, B. E. Wilcomb, F. J. Van Itallie, and R. B. Bernstein, "Formation of Supersonic Beams of Metastable Mercury, $\text{Hg}(6^3P_0)$. Kinetics of Photoexcitation and Intramultiplet Quenching in a Nozzle," *J. Chem. Phys.* **62**, 4466-4473 (1975)
25. H. Horiguchi and S. Tsuchiya, "Quenching of Excited Mercury Atoms (6^3P_1 and 6^3P_0) in Molecular Collisions," *Bull. Chem. Soc. Japan* **47**, 2768-2774 (1974).
26. A. B. Callear, "Excited Mercury Complexes," *Chem. Rev.* **87**, 335-355 (1987)
27. K. Yamanouchi, S. Isogai, S. Tsuchiya, M.-C. Duval, C. Jouvet, O. Benoist d'Azy, and B. Soep, "Structure and Predissociation of Electronically Excited HgN_2 Complex," *J. Chem. Phys.* **89**, 2975-2984 (1988).
28. K. Ohmori, T. Kurosawa, H. Chiba, M. Okunishi, and Y. Sato, "Far-Wing Excitation Study on the Fine-Structure Transition of $\text{Hg}(^3P_1-^3P_0)$ in collisions with N_2 ," *J. Chem. Phys.* **100**, 5381-5383 (1994)
29. M. Okunishi, J. Hashimoto, H. Chiba, K. Ohmori, K. Ueda, and Y. Sato, "Collision-Induced Fine-Structure Transitions of $\text{Hg}(6^3P_1-6^3P_0)$ with N_2 and CO . 1. Initial Orbital Alignment Effects," *J. Phys. Chem. A* **103**, 1734-1741 (1999)
30. P. Lambropoulos, "Topics on Multiphoton Processes in Atoms," *Adv. At. Mol. Phys.* **12**, 87-164 (1976).
31. Ref. 13, Section 6.1.1

32. T. C. James, "Transition Moments, Franck-Condon Factors, and Lifetimes of Forbidden Transitions. Calculation of the Intensity of the Cameron System of CO," *J. Chem. Phys.* **55**, 4118-4124 (1971).
33. T. C. James, "Intensity Measurements of the 0,0 Band of the $a^3\Pi-X^1\Sigma^+$ Cameron System of Carbon Monoxide," *J. Mol. Spectrosc.* **40**, 545-553 (1971).
34. M. E. Rosenkrantz and K. Kirby, "Theoretical study of low-lying $^1\Sigma^-$ and $^1\Delta$ states of CO" *J. Chem. Phys.* **90**, 6528-6532 (1990).
35. R. W. Field, Ph.D. Thesis, Harvard University, 1971.
36. R. T. Jongma, Ph.D. Thesis, University of Nijmegen, The Netherlands, 1997.
37. R. T. Jongma, G. Berden, and G. Meijer, "State-specific lifetime determination of the $a^3\Pi$ state in CO," *J. Chem. Phys.* **107**, 7034-7040 (1997).
38. R.W. Field, O. Benoist d'Azy, M. Lavollé, R. Lopez-Delgado, and A. Tramer, "Radiative Decay Rates from Deperturbed $v = 0 - 7$ Vibrational Levels of CO $A^1\Pi$ Measured Using Synchrotron Radiation", *J. Chem. Phys.* **78**, 2838-2846 (1983).
39. C. V. V. Prasad, G. L. Bhale, and S. Paddi Redd, "The Third Positive ($b^3\Sigma^+ - a^3\Pi_r$) System of CO: Observation of the $v = 2$ Level of $b^3\Sigma^+$," *J. Mol. Spectrosc.* **121**, 261-269 (1987).
40. T. Rytel, "Analysis of the Multiple Perturbation Arising in the $b^3\Sigma^+$ ($v = 0$) State of the CO Molecule," *J. Mol. Spectrosc.* **145**, 420-428 (1991).
41. R. T. Jongma, M. G. H. Boogaarts, and G. Meijer, "Double Resonance Spectroscopy on Triplet States of CO," *J. Mol. Spectrosc.* **165**, 303-314 (1994).
42. C. G. Morgan, M. Drabbels, and A. M. Wodtke, "The Correlated Product State Distribution of Ketene Photodissociation at 308 nm", *J. Chem. Phys.* **104**, 7460-7474 (1996).
43. S. Hayashi, T. M. Mayer, and R. B. Bernstein, "Crossed Molecular Beam Chemiluminescence Study of the Metastable Mercury Reaction: $Hg(^3P_0) + Br_2 \rightarrow HgBr(B) + Br^*$," *Chem. Phys. Lett.* **53**, 419-422 (1978).
44. K. P. Lawley and M. A. D. Fluendy, private communication cited by Hayashi, *et. al.*^[43]
45. C. Kittrell, S. Cameron, L. Butler, R. W. Field, and R. F. Barrow, "Two-Photon Excitation of the $D^1\Delta - X^1\Sigma^+$ Transition in Carbon Monoxide," *J. Chem. Phys.* **78**, 3623-3624 (1983).
46. B. A. Garetz and C. Kittrell, "First Observation of an Identity-Forbidden Transition in Two-Photon Absorption Spectroscopy: $I^1\Sigma^- - X^1\Sigma^+$ Transition in CO," *Phys. Rev. Lett.* **53** 156-158 (1984).
47. C. Kittrell and B. A. Garetz, "Analysis of the $D^1\Delta - X^1\Sigma^+$ Transition in CO Observed by Two-Photon Excitation," *Spectrochim. Acta* **45A**, 31-40 (1989).
48. B. A. Garetz, C. Kittrell, and A. C. Le Floch, "Analysis of the Two-Photon $D^1\Delta - X^1\Sigma^+$ Transition in CO: Perturbations in the (10-0) Band," *J. Chem. Phys.* **94**, 843-853 (1991).
49. C. Kittrell, A. C. Le Floch, and B. A. Garetz, "Analysis of the Two-Photon $D^1\Delta - X^1\Sigma^+$ Transition in CO: II. Perturbations in the (8-0) Band," *J. Phys. Chem.* **97**, 2221-2227 (1993).
50. K. Kirby, M. E. Rosenkrantz, and D. L. Cooper, "The Population of Long-Lived Vibrational Levels of CO: $I^1\Sigma^-$ and $D^1\Delta$," *Phys. Rev. Lett* **68**, 3865-3868 (1992).
51. S. Sekine, Y. Adachi, and C. Hirose, "Optogalvanic Observation of the CO $W^1\Pi - B^1\Sigma^+$ Transition", *J. Chem. Phys.* **90**, 5346-5348 (1989).
52. T. G. Slanger, "Xenon-Sensitized Fluorescence of CO Excited by 1470-Å Radiation," *J. Chem. Phys.* **48**, 586-596 (1968); T. G. Slanger and G. Black, "Resonance Fluorescence and Xenon Sensitization of the CO ($A^1\Pi \rightarrow X^1\Sigma^+$) System," *J. Chem. Phys.* **51**, 4534-4538 (1969).

53. E. Miescher, "Quartet~Doublet Interactions Observed in the Emission Spectrum of the NO Molecule," *J. Chem. Phys.* **73**, 3088-3094 (1980).
54. K. P. Huber and M. Vervloet, "Rotational Analysis of the $b^4\Sigma^-$ - $a^4\Pi_i$ Quartet System of Nitric Oxide," *J. Mol. Spectrosc.* **129**, 1-23 (1988).
55. H. Lefebvre-Brion and F. Guerin, "Calculation of the Radiative Lifetime of the $a^4\Pi$ State of NO," *J. Chem. Phys.* **49**, 1446-1447 (1968).
56. R. A. Copeland, M. J. Dyer, D. L. Huestis, and T. G. Slanger, "The NO ($a^4\Pi$) State: Direct Photoexcitation from the Ground State," *Chem. Phys. Lett.* **236**, 350-354 (1995).
57. M. Drabbels, C. G. Morgan, and A. M. Wodtke, "The Spin-Forbidden $a^4\Pi(v = 13 - 15)$ and $b^4\Sigma^-(v = 3) \leftarrow X^2\Pi(v = 0)$ Bands of Nitric Oxide: A New Scheme for Quantum State-Specific High Resolution Kinetic Energy Measurements," *J. Chem. Phys.* **103**, 7700-7707 (1995).
58. P. C. Cosby, R. A. Copeland, D. G. Williamson, G. Gaudin, M. J. Dyer, D. L. Huestis, and T. G. Slanger, "The NO ($a^4\Pi$) State: Spectroscopy of the $a^4\Pi_i-X^2\Pi_r$ 11-0 Band," *J. Chem. Phys.* **107**, 2249-2256 (1997).
59. R. A. Copeland, M. J. Dyer, H. I. Bloemink, and T. G. Slanger, "The NO ($a^4\Pi$) State: Collisional Removal of $v = 11$ and $a^4\Pi \sim B^2\Pi$ Interactions," *J. Chem. Phys.* **107**, 2257-2266 (1997).
60. M. J. Dyer, G. W. Faris, P. C. Cosby, D. L. Huestis, and T. G. Slanger, "Optical Excitation of the $b^4\Sigma^- \leftarrow X^2\Pi$ Transition in NO," *Chem. Phys.* **171**, 237-252 (1993).
61. P. C. Cosby and T. G. Slanger, "External Magnetic Field Effects in NO ($B^2\Pi$), $B^2\Pi \sim a^4\Pi$ Coupling, and $b^4\Sigma^-$ and $a^4\Pi$ Level Positions," *J. Chem. Phys.* **95**, 2203-2205 (1991).
62. M. Ogawa, "The Band Spectrum of Nitric Oxide in the Near Infrared Region," *Sci. of Light* **3**, 39-46 (1954).
63. R. J. Fallon, J. T. Vanderslice, and E. A. Mason, "Quenching of Excited $Hg(^3P_1)$ by NO," *J. Phys. Chem.* **63**, 2082-2083 (1959).
64. O. P. Strausz and H. E. Gunning, "The $Hg(^3P_1)$ -Photosensitized Decomposition of Nitric Oxide," *Canad. J. Chem.* **39**, 2549-2555 (1961).
65. G. Karl, P. Kruus, J. C. Polanyi, and I. M. W. Smith, "Infrared-Emission Studies of Electronic-to-Vibrational Energy Transfer. III. $Hg^* + NO$," *J. Chem. Phys.* **46**, 244-253 (1967).
66. Ch. Ottinger and A. F. Vilesov, "Intramolecular Collisional Transfer in NO ($a^4\Pi \rightarrow B^2\Pi$, $b^4\Sigma^-$): Gateway-Type, Resonant Versus Direct, Nonresonant Mechanisms", *J. Chem. Phys.* **100** 1805-1814 (1994); *ibid*, "Lifetime Measurements on Perturbed Levels of NO($B^2\Pi$) and Precise Term Energy of the NO($a^4\Pi$) State", *J. Chem. Phys.* **100**, 1815-1822 (1994).
67. W. A. Noyes, Jr., "Photochemical Studies. XII. The Photochemical Reaction between Nitric Oxide and Mercury Vapor," *J. Am. Chem. Soc.* **53**, 514-526 (1931).
68. M. Z. Hoffman and R. B. Bernstein, "The $Hg(^3P_1)$ -Photosensitized Decomposition of Nitric Oxide," *J. Phys. Chem.* **64**, 1769-1771 (1960).
69. G. Karl and J. C. Polanyi, "Infrared Emission Arising from Electronic-Vibrational Energy Transfer: $Hg^* + CO$," *J. Chem. Phys.* **38**, 271-272 (1963).
70. M. R. Taherian, P. C. Cosby, and T. G. Slanger, "Detection and Characterization of the NO ($L'^2\Phi$) State at 6.6 eV," *J. Chem. Phys.* **83**, 3878-3887 (1985).
71. M. Huber, "Excited States and Rydberg Series in the Emission Spectrum of NO," *Helv. Phys. Acta* **37**, 329-347 (1964).

72. K. P. Huber and G. Herzberg, "Constants of Diatomic Molecules," van Nostrand Reinhold, New York, 1979.
73. R. A. Young and R. L. Sharpless, "Chemiluminescent Reactions Involving Atomic Oxygen and Nitrogen," *J. Chem. Phys.* **39**, 1071-1102 (1963).
74. A. R. W. McKellar, N. H. Rich, and H. L. Welsh, "Collision-Induced Vibrational and Electronic Spectra of Gaseous Oxygen at Low Temperatures," *Can. J. Phys.* **50**, 1-9 (1972); A. J. Blake and D. G. McCoy, "The Pressure Dependence of the Herzberg Photoabsorption Continuum of Oxygen," *J. Q. R. S. T.* **38**, 113-120 (1987).
75. S. H. Whitlow and F. D. Findlay, "Single and Double Transitions in Molecular Oxygen," *Can. J. Chem.* **45**, 2087-2091 (1967).
76. T. Ishiwata, A. Ishiguro, and K. Obi, "Optical-Optical Double Resonance Spectroscopy of Cl₂: Analysis of the A³Π(1_u)–X¹Σ_g⁺ System," *J. Mol. Spectrosc.* **147**, 300-320 (1991); *ibid*, "Optical-Optical Double Resonance Spectroscopy of Cl₂: Analysis of the 1_g(³P₂) – A³Π(1_u) System," *J. Mol. Spectrosc.* **147**, 321-333 (1991); J.-H. Si, T. Ishiwata, and K. Obi, "Optical-Optical Double Resonance Spectroscopy of Cl₂: Absolute Position of the Lowest-Lying 2_g (³P₂) Ion-Pair State," *J. Mol. Spectrosc.* **147**, 334-345 (1991).
77. T. Ishiwata, Y. Kasai, and K. Obi, "Optical-Optical Double Resonance Spectroscopy of Cl₂: First Observation and Analysis of the 0⁻(³P₁) Ion-Pair State and the Lower-Lying B' ³Π(0_u⁻) Valence State," *J. Chem. Phys.* **95**, 60-65 (1991).
78. T. Ishiwata, J.-H. Si, and K. Obi, "Optical-Optical Double Resonance Spectroscopy of Cl₂: Analysis of the 1_g (³P₁) – A³Π(1_u) System," *J. Chem. Phys.* **96**, 5678-5686 (1992).
79. T. Ishiwata, Y. Kasai, and K. Obi, "Observation of the 0_u⁻ (³P₁) Ion-Pair state of Cl₂ by Perturbation-Facilitated Optical-Optical Double Resonance," *Chem. Phys. Lett.* **261**, 175-180 (1996).
80. P. C. Tellinghuisen, B. Guo, D. K. Chakraborty, and J. Tellinghuisen, "The D'–A' Transition in Cl₂" *J. Mol. Spectrosc.* **128**, 268-277 (1988).
81. W. E. Kammer, "Ab Initio SCF and CI Calculations of Linear and Bent Acetylene," *Chem. Phys. Lett.* **6**, 529-532 (1970); D. Demoulin, "The Shape of Some Excited States of Acetylene," *Chem. Phys.* **11**, 329-341 (1975); R.W. Wetmore, and H.F. Schaefer, "Triplet Electronic States of Acetylene: Cis and Trans Structures and Energetics," *J. Chem. Phys.* **69**, 1648-1654 (1978); H. Lischka, and A. Karpfen, "Ab Initio Calculations on the Excited-States of Pi-Systems. 1. Valence Excitations in Acetylene," *Chem. Phys.* **102**, 77-89 (1986); G. Vacek, J. R. Thomas, B. J. DeLeeuw, Y. Yamaguchi, and H. F. Schaefer III, "Isomerization Reactions on the Lowest Potential Energy Hypersurface of Triplet Vinylidene and Triplet Acetylene," *J. Chem. Phys.* **98**, 4766-4776 (1993); Y. Yamaguchi, G. Vacek, and H. F. Schaefer III, "Low-Lying Triplet Electronic States of Acetylene: cis ³B₂ and ³A₂, trans ³B_u and ³A_u" *Theor. Chim. Acta* **86**, 97-113 (1993); Y. Yamaguchi, G. Vacek, J. R. Thomas, B.J. DeLeeuw, and H. F. Schaefer III, "First and Second Energy Derivative Analyses of the Vinylidene and Acetylene Triplet State Potential Energy Surfaces," *J. Chem. Phys.* **100**, 4969-4980 (1994). C. D. Sherrill, G. Vacek, Y. Yamaguchi, and H. F. Schaefer III, "The \tilde{A}^1A_u State and the T₂ Potential Surface of Acetylene: Implications for Triplet Perturbations in the Fluorescence Spectra of the \tilde{A} -State," *J. Chem. Phys.* **104**, 8507-8515 (1996); G. Vacek, C.D. Sherrill, Y. Yamaguchi, and H.F. Schaefer, III, "The Anomalous Behavior of the Zeeman Anticrossing Spectra of \tilde{A}^1A_u Acetylene: Theoretical Considerations," *J. Chem. Phys.* **104**, 1774-1778 (1996);
82. C. S. Burton and H. E. Hunziker, "Triplet State of Acetylene: Biacetyl Emission from the Mercury Photosensitized Reaction," *J. Chem. Phys.* **57**, 339-347 (1972).
83. H.R. Wendt, H. Hippler, and H.E. Hunziker, "Triplet Acetylene: Near Infrared Electronic Absorption Spectrum of the cis Isomer, and Formation from Methylene," *J. Chem. Phys.* **70**, 4044-4048 (1979);

84. H. Kanamori, "Hydrocarbonated Radicals with a C=C Core," Talk WA2, 53rd International Symposium on Molecular Spectroscopy, Ohio State University, 1998; K. Tanigawa and H. Kanamori, "High Resolution Study of Triplet Acetylene," Talk FD3, 50th International Symposium on Molecular Spectroscopy, 1995.
85. Q. Cui, K. Morokuma, and J. F. Stanton, "Ab Initio MO Studies on the Photodissociation of C₂H₂ from the S₁ (¹A_u) State. Non-Adiabatic Effects and S~T Interaction," *Chem. Phys. Lett.* **263**, 46-53 (1996).
86. Q. Cui, K. Morokuma, and J. F. Stanton, "Ab Initio MO Studies on the Photodissociation of C₂H₂ from the S₁ (¹A_u) State. II. Mechanism Involving Triplet States," *Chem. Phys. Lett.* **272**, 319-327 (1997).
87. P. Swiderek, M. Michaud, and L. Sanche, "Condensed Phase Electron-Energy-Loss Spectroscopy of the Low-Lying Triplet States of Acetylene," *J. Chem. Phys.* **106**, 9403-9410 (1997); K. Malsch, R. Rebentisch, P. Swiderek and G. Hohlneicher, "Excited States of Acetylene: a CASPT2 Study," *Theor. Chem. Accts.* **100**, 171-182 (1998).
88. D. G. Wilder, P. J. Hicks, and J. Comer, "An Electron Impact Energy-Loss Study of Triplet States of Acetylene," *J. Phys. B.* **10**, L403-L407 (1977).
89. W. M. Flicker, O. A. Mosher, and A. Kupperman, "Singlet→Triplet Transitions in Methyl-Substituted Ethylenes," *Chem. Phys. Lett.* **36**, 56-60 (1975).
90. E. H. Van Veen, "Low-Energy Electron-Impact Spectroscopy on Ethylene," *Chem. Phys. Lett.* **41**, 540-543 (1976).
91. L. Serrano-Andrés, M. Merchán, I. Nebot-Gil, R. Lindh, and B. O. Roos, "Towards an Accurate Molecular Orbital Theory for Excited States: Ethene, Butadiene, and Hexatriene," *J. Chem. Phys.* **98**, 3151-3162 (1992).
92. B. Gemein and S. D. Peyerimhoff, "Radiationless Transitions between the First Excited Triplet State and the Singlet Ground State in Ethylene: A Theoretical Study," *J. Phys. Chem.* **100**, 19257-19267 (1996).
93. D. Danovich, C. M. Marian, T. Neuheuser, S. D. Peyerimhoff, and S. Shaik, "Spin-Orbit Coupling Patterns Induced by Twist and Pyramidalization Modes in C₂H₄: A Quantitative Study and a Qualitative Analysis," *J. Phys. Chem. A* **102**, 5923-5936 (1998).
94. S. El-Taher, R. H. Hilal, and T. A. Albright, "An Ab Initio Study of Structures and Energetics of the Planar Ground and 90°-Twisted Excited States of Substituted Ethylenes," *Int. J. Quantum Chemistry* **82**, 242-254 (2001).
95. D. W. Setser, B. S. Rabinovitch, and D. W. Placzek, "Intramolecular Hydrogen Migration and Decomposition in the Hg(³P₁) Photosensitization of trans-Ethylene-d₂," *J. Am. Chem. Soc.* **85**, 862-866 (1963).
96. H. E. Hunziker, "Cadmium-Photosensitized Interconversion of *cis*-, *trans*-, and *geminal*-Ethylene-d₂," *J. Chem. Phys.* **50**, 1288-1294 (1969).
97. S. Dushman and J. M. Lafferty, "Scientific Foundations of Vacuum Technique," John Wiley and Sons, New York, 1962.
98. C.M. Gittins, N.A. Harris, Ma Hui, and R.W. Field, "Ionization-Detected Optical-Optical Double Resonance Spectroscopic Studies of Moderate Energy Rydberg States of Calcium Monofluoride," *Canad. J. Phys.* **79**, 247-286 (2001).
99. H. Ishikawa and W. A. Noyes, "Photosensitization by Benzene Vapor: Biacetyl. The Triplet State of Benzene," *J. Chem. Phys.* **37**, 583-591 (1962).

100. C. S. Burton and H. E. Hunziker, "Gas Phase Absorption Spectra and Decay of Triplet Benzene, Benzene-d₆, and Toluene," *Chem. Phys. Lett.* **6**, 352-358 (1970).
101. R. S. Freund and W. Klemperer, "Radio-Frequency Spectrum of the a³II State of Carbon Monoxide," *J. Chem. Phys.* **43**, 2422-2428 (1965); R. S. Freund and W. Klemperer, "Molecular Beam Time-of-Flight Measurements for the Study of Metastable and Repulsive Electronic States," *J. Chem. Phys.* **47**, 2897-2904 (1967).
102. R. Chance, A. Prock, and R. Silbey, "Molecular Fluorescence and Energy Transfer near Interfaces," *Adv. Chem. Phys.* **37**, 1-65 (1978).
103. G. T. Fraser and B. H. Pate, "The Molecular Stark Effect in Regions of High State Density: Overall Simplicity and Underlying Complexity in the Response to a Static Electric Field," *J. Chem. Phys.* **100**, 6210-6220 (1994).
104. N. R. Pillsbury, J. Choo, J. Laane, and S. Drucker, "The Lowest n, π^* Triplet State of 2-Cyclopenten-1-one: Cavity Ringdown Absorption Spectrum and Ring-Bending Potential Energy Function," *J. Phys. Chem. A* **107**, 10648-10654 (2003).
105. J. Choo, S. Kim, S. Drucker, and J. Laane, "Density Functional Calculations, Structure, and Vibrational Frequencies of 2-Cyclopenten-1-one in its S₀, S₁(n, π^*), and T₁(n, π^*) States," *J. Phys. Chem. A* **107**, 10655-10659 (2003).
106. J.M. Lisy and W. Klemperer, "Electric Deflection Studies of Metastable Acetylene," *J. Chem. Phys.* **72**, 3880-3883 (1980).
107. J.K. Lundberg, R.W. Field, C.D. Sherrill, E.T. Seidl, Y. Xie, and H.F. Schaefer III, "Acetylene: Synergy Between Theory and Experiment," *J. Chem. Phys.* **98**, 8384-8391 (1993).
108. E. Murad, "Spacecraft Interaction with Atmospheric Species in Low Earth Orbit," *J. Spacecraft and Rockets* **33**, 131-136 (1996).
109. R. A. Viereck, E. Murad, D. J. Knecht, and C. P. Pike, "The Interaction of the Atmosphere with the Space Shuttle Thruster Plume: The NH (A-X) 336nm Emission," *J. Geophys. Res.* **101**, A3, 5371-5380 (1996).
110. "Infrared Spectral Data Analysis and Remote Sensing Using Pattern Recognition Algorithms" S.J. Lipson, R.B. Lockwood, D.L. Vititoe, C. L. Allred, W.A.M. Blumberg, P.S. Armstrong, M.P. Jacobson, S.L. Coy, and R.W. Field, Presented at the University of Virginia Physics Department Atomic and Molecular Seminar (Charlottesville, VA, April 1997); - Invited; "Infrared Spectral Data Analysis and Remote Sensing Using Pattern Recognition Algorithms" S.J. Lipson, R.B. Lockwood, D.L. Vititoe, C. L. Allred, W.A.M. Blumberg, P.S. Armstrong, M.P. Jacobson, S.L. Coy, and R.W. Field, Presented at the 1997 Spring Meeting of the American Geophysical Union (Baltimore, MD, May 1997); "Disentangling Vibrational Bands in CO Spectra Utilizing Spectroscopic Pattern Recognition Techniques" M.P. Jacobson, S.L. Coy, R.W. Field, S.J. Lipson, R.B. Lockwood, D.L. Vititoe, W.A.M. Blumberg, and P.S. Armstrong, Presented at the 52nd International Symposium on Molecular Spectroscopy (Columbus, OH, June 1997); "Infrared Spectral Data Analysis and Remote Sensing Using Pattern Recognition Algorithms" S.J. Lipson, R.B. Lockwood, D.L. Vititoe, C. L. Allred, W.A.M. Blumberg, P.S. Armstrong, M.P. Jacobson, S.L. Coy, and R.W. Field, Presented at the 20th Annual Review Conference of Atmospheric Transmission Models (Hanscom AFB, MA, June 1997); "Techniques for Target Detection Using Hyperspectral Data" C. L. Allred, D.L. Vititoe, S.J. Lipson, R.B. Lockwood, L. S. Jeong, W.A.M. Blumberg, P.S. Armstrong, M.P. Jacobson, S.L. Coy, R.W. Field, and W.J. Marinelli, Presented at the Spectral Imaging Technology Workshop (Kirtland AFB, NM, August 1997); "Techniques for Target Detection Using Hyperspectral Data" D.L. Vititoe, C. L. Allred, S.J. Lipson, R.B. Lockwood, L. S. Jeong, W.A.M. Blumberg, P.S. Armstrong, M.P. Jacobson, S.L. Coy, and R.W. Field Presented at the Defense Intelligence Agency Advanced Concepts Division 1997 Spectroradiometric Symposium (San Diego, CA, November 1997); "Atmospheric Remote Sensing Applications of Spectroscopic Pattern Recognition Algorithms" D.L. Vititoe, S.J. Lipson, C. L. Allred, R.B. Lockwood,

- W.A.M. Blumberg, P.S. Armstrong, M.P. Jacobson, S.L. Coy, and R.W. Field, Presented at the 1997 Fall Meeting of the American Geophysical Union (San Francisco, CA, December 1997).
111. S. L. N. G. Krishnamachari and R. Venkatasubramanian, "A Transient Absorption Spectrum Attributable to the Triplet-Triplet Transition of HCN," *Spect. Lett.* **17**, 401-407 (1984).
 112. S.L.N.G. Krishnamachari and R. Venkatasubramanian, "Electronic Absorption Spectra of HNC and DNC," *Spect. Lett.* **19**, 55-60 (1986).
 113. W. D. Laidig and H. F. Schaefer III, "Some Characteristics of the Intravalence Triplet-Triplet Electronic Transition in HCN," *J. Chem. Phys.* **73**, 1470-1472 (1980).
 114. S.-C. Woo and T.-K. Liu, "The New Absorption System of Cyanogen Gas in the Near Ultraviolet. System I," *J. Chem. Phys.* **5**, 161-165 (1937).
 115. J. H. Callomon and A. B. Davey, "Rotational Analysis of the 3000-Å Absorption System of Cyanogen, C₂N₂," *Proc. Phys. Soc.* **82**, 335-336 (1963).
 116. G. J. Cartwright, D. O. O'Hare, A. D. Walsh, and P. A. Warsop, "The Rotational and Vibrational Structure of the 2500 Å System of Cyanogen," *J. Mol. Spectrosc.* **39**, 393-399 (1971).
 117. S. A. Barts and J. B. Halpern, "The Emission Spectrum of C₂N₂," *Chem. Phys. Lett.* **161**, 207-211 (1989).
 118. J. B. Halpern and Y. Huang, "Radiative Lifetimes, Fluorescence Quantum Yields and Photodissociation of the C₂N₂ ($\tilde{A}^1\Sigma_u^-$) and ($B^1\Delta_u$) States: Evidence for Sterically Hindered, Triplet Mediated Crossings to the ($\tilde{X}^1\Sigma_g^+$) Ground State," *Chem. Phys.* **222**, 71-86 (1997).
 119. S.-C. Woo and T.C. Chu, "The Absorption Spectrum of Diacetylene in the Near Ultraviolet," *J. Chem. Phys.* **3**, 541-543 (1935).
 120. S.-C. Woo and T.C. Chu, "The Absorption Spectrum of Diacetylene in the Near Ultraviolet. II," *J. Chem. Phys.* **5**, 786-791 (1937).
 121. R. E. Bandy, C. Lakshminarayan, and T. S. Zwier, "Spectroscopy and Photophysics of the $^1\Delta_u \leftarrow ^1\Sigma_g^+$ Transition in Jet Cooled C₄H₂, C₄HD, and C₄D₂," *J. Phys. Chem.* **96**, 5337-5343 (1992).
 122. R. E. Bandy, C. Lakshminarayan, R. K. Frost, and T. S. Zwier, "Direct Detection of C₄H₂ Photochemical Products: Possible Routes to Complex Hydrocarbons in Planetary Atmospheres," *Science*, **258**, 1630-1633 (1992).
 123. F.C. Hagemeister, C.A. Arrington, B.J. Giles, B. Quimpo, L. Zhang, and T.S. Zwier, "Cavity Ringdown Methods for Studying Intramolecular and Intermolecular Dynamics", ACS Symposium Series **720** (Cavity Ringdown Spectroscopy), 210-232 (1999).
 124. S. Glickler and H. Okabe, "Photochemistry of Diacetylene," *J. Phys. Chem.* **91**, 437-440 (1987).
 125. V. A. Job and G. W. King, "The Electronic Spectrum of Cyanoacetylene, Part I. Analysis of the 2600-Å System," *J. Mol. Spectrosc.* **19**, 155-177 (1966); V. A. Job and G. W. King, "The Electronic Spectrum of Cyanoacetylene, Part II. Analysis of the 2300-Å System," *J. Mol. Spectrosc.* **19**, 178-184 (1966).
 126. W. T. Raynes, "Rotational Analysis of Some Bands of the Triplet-Singlet Transition in Formaldehyde," *J. Chem. Phys.* **44**, 2755-2777 (1966).
 127. F. W. Birss, R. Y. Dong, and D. A. Ramsay, "Molecular Constants for the \tilde{a}^3A_2 State of Formaldehyde," *Chem. Phys. Lett.* **18**, 11-13 (1973).
 128. J. M. Brown, A. D. Buckingham, and D. A. Ramsay, "High Resolution Studies of Magnetic Optical Activity in the $^3A_2 - ^1A_1$ System of Formaldehyde," *Can. J. Phys.* **54**, 895-906 (1976).

129. F. W. Birss, D. A. Ramsay, and S. M. Till, "Singlet-Triplet Perturbations in Formaldehyde," *Chem. Phys. Lett.* **53**, 14-17 (1978).
130. C. M. L. Kerr, D. C. Moule, and D. A. Ramsay, "The Magnetic Rotation Spectrum of Formaldehyde: Singlet-Triplet Perturbations in the 2^1A_1 , 2^1A_3 , 2^2A_3 , and 2^3A_1 Levels of the \tilde{A}^1A_2 State of H_2CO ," *Can. J. Phys.* **61**, 6-14 (1982).
131. S. R. Langhoff and E. R. Davidson, "Ab Initio Evaluation of the Fine Structure and Radiative Lifetime of the 3A_2 ($n \rightarrow \pi^*$) State of Formaldehyde," *J. Chem. Phys.* **64**, 4699-4710 (1976).
132. J. C. D. Brand, J. H. Callomon, and J. K. G. Watson, "The $3820\text{-}\text{\AA}$ $^1A'' \leftarrow ^1A'$ Transition of Propynal," *Can. J. Phys.* **39**, 1508-1510 (1961).
133. E. J. Bair, W. Goetz, and D. A. Ramsay, "Magnetic Rotation and Absorption Spectra of *cis* and *trans* Acrolein," *Can. J. Phys.* **49**, 2710-2717 (1971).
134. G. A. Osborne and D. A. Ramsay, "Near Ultraviolet Absorption Spectra of *cis* and *trans* Acrolein and Acrolein- d_1 ," *Can. J. Phys.* **51**, 1170-1175 (1973).
135. S. Altunata and R. W. Field, "A Statistical Approach to the Study of the Singlet-Triplet Interactions in the 5.5 – 5.7 eV Region of Acetylene," *J. Chem. Phys.* **113**, 6640-6651 (2000).
136. S. Altunata and R. W. Field, "An Assumption-Violating Application of the Lawrance-Kinght Deconvolution Procedure: A Retrieval of Electronic Coupling Mechanisms Underlying Complex Spectra," *J. Chem. Phys.* **114**, 6557-6561 (2001).
137. M. Drabbels, J. Heinz, and W. L. Meerts, "A study of the Singlet-Triplet Perturbations in the \tilde{A}^1A_u State of Acetylene by High Resolution Ultraviolet Spectroscopy," *J. Chem. Phys.* **100** 165-174 (1994).

III. AFOSR Supported Publications (since 1999)

1. M.P. Jacobson, S.L. Coy, R.W. Field, S.J. Lipson, R.B. Lockwood, D.L. Vitito, W.A.M. Blumberg, and P.S. Armstrong, "Numerical Pattern Recognition Analysis of CO Atmospheric Simulation Experiments," *J. Chem. Phys.* **104**, 249-257 (2000).
2. H. Ishikawa, R.W. Field, S.C. Farantos, M. Joyeux, J. Koput, C. Beck, and R. Schinke, "HCP→CPH Isomerization: Caught in the Act!," *Annu. Revs. Phys. Chem.* **50**, 443-484 (1999).
3. M. Joyeux, D. Sugny, V. Tyng, M.E. Kellman, H. Ishikawa, R.W. Field, C. Beck, and R. Schinke, "Semiclassical Study of the Isomerization States of HCP," *J. Chem. Phys.* **112**, 4162-4172 (2000).
4. A.F. Ruckstuhl, M.P. Jacobson, R.W. Field, and J.A. Dodd, "Baseline Subtraction Using Robust Local Regression Estimation," *J. Quant. Spectr. Radiat. Transf.* **68**, 179-193 (2001).
5. S. Altunata and R. W. Field, "A Statistical Approach to the Study of the Singlet-Triplet Interactions in the 5.5 – 5.7 eV Region of Acetylene," *J. Chem. Phys.* **113**, 6640-6651 (2000).
6. E. S. Hwang, J. B. Lipson, R.W. Field, and J. A. Dodd, "Detection of OH (X, v) via the $B^2\Sigma^+ - X^2\Pi$ Transition and Properties of the $B^2\Sigma^+$ State," *J. Phys. Chem.* **105**, 6030 – 6037 (2001).
7. M. Silva, R. Jongma, R.W. Field, and A.M. Wodtke, The Dynamics of 'Stretched Molecules': Experimental Studies of Highly Vibrationally Excited Molecules with Stimulated Emission Pumping," *Ann. Rev. Phys. Chem.* **52**, 811-852 (2001).
8. S. Altunata and R. W. Field, "An Assumption-Violating Application of the Lawrance-Kinght Deconvolution Procedure: A Retrieval of Electronic Coupling Mechanisms Underlying Complex Spectra," *J. Chem. Phys.* **114**, 6557-6561 (2001).

9. S. Altunata, K. L. Cunningham, M. Canagaratna, R. Thom and R. W. Field, "The Mechanism of Surface Electron Ejection by Laser Excited Metastable Molecules," *J. Phys. Chem.* **106**, 1122-1130 (2002).
10. A. P. Mishra, R. L. Thom, and R. W. Field, "New S_1 State Vibrational and $T_{3,2,1}$ Spin-Rotational Assignments in the Vicinity of the $\tilde{A}^1X_u - \tilde{X}^1\Sigma_g^+ V_0^3 K_0^1$ Band," *J. Mol. Spectrosc.* **228**, 565-579 (2004).
11. A. P. Mishra, R. L. Thom, S. Altunata, and R. W. Field, "Study of Intramolecular Dynamics of Highly Energized Small Molecules Using Laser Spectroscopic Techniques," in *Current Developments in Atomic, Molecular, and Chemical Physics with Applications* (ed. Man Mohan), 2003, Kluwer, New York.
12. A. P. Mishra, R. W. Field, S. V. N. Bhaskara Rao, R. D'Souza, and T. K. Balasubramanian, "Absorption Intensities of the Multipole-Field-Induced Zero-Phonon Transitions in Solid HD, HT, and DT," *Phys. Rev. B.* **67**, 134305:1-9 (2003).
13. A. P. Mishra and R. W. Field, "Absorption Intensities of the Multipole-Field-Induced Double Transitions Involving a Homonuclear-Heteronuclear Pair of Hydrogen Molecules in Condensed Phase," *Phys. Rev. B.* **68**, 184303:1-8 (2003).
14. H. Lefebvre-Brion and R. W. Field, "The Spectra and Dynamics of Diatomic Molecules," Elsevier, 2004.

IV. Interactions/Transitions: Talks

Talks

Talks by RWF on the triplet project at Argonne National Laboratory (10/9/00), University of California Riverside (12/7/00), Pacificchem Honolulu (12/15/00), University of Minnesota (4/11/01), Tsinghua University, Beijing (5/9/01), AFOSR Molecular Dynamics (5/21/01), Molecular Spectroscopy Symposium at Ohio State (6/13/01), University of Pennsylvania (2/28/02), Caltech (6/4/02), EPENS at Montauk (9/24/02).

Talks by Selen Altunata on the triplet project at Wesleyan University (10/31/00), LAM Electronics, IGEN.

Talks By Ryan Thom, Molecular Spectroscopy Symposium at Ohio State (6/12/01 and 6/19/02).

Ph.D. Theses

Selen Altunata, "Intersystem Crossing in Acetylene: A Mechanistic Study"

<http://rwf.lms.mit.edu/group/theses/selen-theses.pdf>

Kevin Cunningham, "The Surface Ejection of Electrons by Laser Excited Metastables Spectroscopy of Acetylene"

<http://rwf.lms.mit.edu/group/theses/kevin-theses.pdf>

V. New Discoveries, Inventions, Patents

None.

VI. Honors

Robert W. Field: Elected Fellow of the American Association for the Advancement of Science (AAAS) 2002. AFRL, Space Vehicles Directorate: "Team Publication of the Year" for 2000: (M.P. Jacobson, S.L. Coy, R.W. Field, S.J. Lipson, R.B. Lockwood, D.L. Vittoe, W.A.M. Blumberg, and P.S. Armstrong, "Numerical Pattern Recognition Analysis of CO Atmospheric Simulation Experiments," *J. Phys. Chem.* **104**, 249-257 (2000).)